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## 13. ABSTRACT (Maximum 200 words)

In this project we seek to use this variability of solvating power to dissolve high molecular weight polymers, provide solution processing capacity for polymers which are typically difficult to process, and produce blends of normally incompatible polymers from cosolvated mixtures. This last area, polymer blends, is one of great potential and interest because traditional polymer blends are often phase separate into large domains. For example, we expect that by molecularly blending a liquid crystallize polymer with long chain, fiber forming, crystalline polymers, we will reduce the macroscopic phase separation that now limits effective utilization of both the LCP reinforcement and the matrix polymer processibility.

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OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Grant/Contract N00014-89-J-3063

R&T Code 4132041

PROCESSING OF POLYMERS USING SUPERCRITICAL FLUIDS

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OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

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Contract/Grant Number: N00014-89-J-3063  
Contract/Grant Title: Processing of Polymers Using Supercritical Fluids  
Principle Investigators: John J. Aklonis and Eric J. Amis  
Mailing Address: Department of Chemistry  
University of Southern California  
Los Angeles, CA 90089-0482

a. Number of papers submitted to refereed journals, but not yet published: 0  
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h. Number of invited presentations at workshops or professional society meetings: 2  
i. Number of presentations at workshops or professional society meetings: 3  
j. Honors/Awards/Prizes for contract/grant employees (list attached): 8

- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:

Graduate Students:	3
Post-Doctoral Associates/Visiting Scholars:	6
including the number of,	
Female Graduate Students:	1
Female Post-Doctoral Associates:	0
the number of,	
Minority Graduate Students:	0
Minority Post-Doctoral Associates:	0
and the number of,	
Asian Graduate Students:	1
Asian Post-Doctoral Associates:	1

- l. Other funding:

Agency	Title	Received this year	Total award	Period of performance	Relationship to this grant
Department of Energy (EJA: co-PI)	Synthesis of Novel Associating Water Soluble Copolymers	85,681	315,488	8/89 - 7/92	none
Department of Education (EJA: PI)	Graduate Fellowships in Areas of National Need (Chemistry)	223,000	669,000	1/90 - 12/92	Student support for department
PRF(ACS) (EJA: PI)	Kinetics of Polymer Crystallization from Solution	20,000	40,000	5/91 - 8/93	none
Department of Education (EJA: PI)	Graduate Fellowships in Areas of National Need (Chemistry)	147,876	443,628	9/91 - 8/94	Student support for department
Applied Biosystems (EJA: PI)	Characterization of Novel Gels for DNA Sequencing	68,919	68,919	3/92 - 2/93	none

**J. Honors/Awards/Prizes for contract/grant employees**

- |                           |   |
|---------------------------|---|
| <b>Eric J. Amis</b>       | <b>Appointed as the new Editor of the <i>Journal of Polymer Science: Polymer Physics Edition</i></b><br><b>Appointed Faculty Associate Fellow of the Loker Hydrocarbon Research Institute</b><br><b>Chairman, American Physical Society Polymer Physics Division Publications Committee and Guest Editor of December 1992 <i>Journal of Polymer Science: Polymer Physics Edition</i></b><br><b>Co-Chair, APS Polymer Physics Membership Committee</b> |
| <b>Marián Sedlák</b>      | <b>Appointed Chairman, Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, Kosice, Czechoslovakia</b>  |
| <b>Diane Valachovic</b>   | <b>US Department of Education Graduate Student Fellowship</b>   |
| <b>Ning Hu</b>            | <b>Moulton Graduate Fellowship</b>  |
| <b>Thomas A. P. Seery</b> | <b>US Department of Education Graduate Student Fellowship</b>   |

## Office of Naval Research

### Processing of Polymers Using Supercritical Fluids

#### Proposed work

A primary goal of polymer chemists has been the search for new materials with unique properties. By one path a synthetic chemist utilizes his knowledge of chemistry to vary the structure of a monomer or to modify a polymer to vary its properties. By another path methods are developed for preparing polymer blends with properties distinct from the parent polymers. Due to the low entropy of mixing in polymer systems specific enthalpic interactions are necessary to form single phase materials. The number of polymer blends where these enthalpic interactions are favorable is small.[1,2] The important factor in blending polymers is therefore the ability to control the phase morphology of an incompatible polymer blend. This usually involves the mixing of polymers by use of cosolvents, blending with a block copolymer compatibilizer, or by carefully determined heating, mixing, and quenching sequences.[1,2]

Solution casting of films composed of incompatible polymers using a mutual good solvent is a well known manner for the examination of morphology. However, conventional evaporation of solvent results in only a limited ability to control the degree to which phase separation occurs. The morphology can be controlled somewhat by the use of vacuum or heat, however film quality can be compromised by bubbling associated with a phase transition of the solvent from liquid to gas.

Supercritical fluids represent a state of matter with properties intermediate between those of a gas and a liquid. Since a supercritical fluids cohesive energy density varies with pressure, the solvents solvating power can be smoothly varied without the occurrence of a phase transition. This has been utilized in a numbers of processes such as the well known carbon dioxide extraction of caffeine from coffee beans. For the preparation of blended polymers we can carefully utilize pressure drops to control the degree to which phase separation proceeds, such as expansion of a solution through a nozzle. Since supercritical fluids have transport properties similar to those of a gas removal of solvent can proceed rapidly. As such supercritical fluids present the opportunity to develop unique techniques for blending and processing polymers.

Perhaps the most elegant use of a supercritical fluid's variable solvation power in the polymer field was the chromatographic separation of styrene oligomers through capillary tubing using pentane as a solvent by Jantoft and Gouw.[3] By performing a programmed increase in the fluids pressure from 28 to 85 bar selective solubilization of increasing oligomer size was achieved. Clean separation of oligomers up to degree of polymerization 30 was possible, with some separation up to DP 40. High solubilities are not required for chromatography so addition of a non-solvent for polystyrene, methanol, modifier helped increase the resolution for these oligomers.

Of special interest to us was the potential for processing polymers normally considered difficult using the solvation power of supercritical fluids. This includes the large number of high performance polymers that do not soften or flow even at temperatures approaching their degradation temperatures.[4,5] However, the solvent assisted formation of polymer blends of these materials is difficult since they are soluble in only the most powerful solvents such as fuming sulfuric acid and methane sulfonic acid. The use of strong acid solvents also prevents their blending with less robust amorphous materials. Blend quenching from these solvents is also difficult.

When this grant proposal was initially submitted there were few reported instances of supercritical fluids being used to blend, mix, or process polymers.[6-8] Since then several reports have been published on the phase behavior of various polymers in critical and sub critical fluids. These include the systems polystyrene in butane and pentane,[9] polyethylene in propane,[10] and copolymers of polyethylene in propane.[11] It also includes recent work by DeSimone et al. showing that polymers produced from perfluoro alkyl acrylate monomers are soluble in supercritical CO<sub>2</sub>. [12] These results and our work indicate that potential exists for the use of supercritical fluid solvents in carefully selected systems.

### **Work Accomplished**

The use of supercritical solvents to process polymers relies on a thorough understanding of solubility over the readily accessible pressure and temperature range of the fluid. We have therefore chosen to investigate a wide range of solvent-polymer pairs in an effort to identify the criteria governing the interactions of supercritical fluids with polymers. The properties of high performance polymers are largely controlled by their rigid-rod structure and

large cohesive energy density which leads to highly crystalline material. These two factors impart the incredible mechanical properties and thermal stability to these polymer systems, however they also lead to their limited solubility. The strong solvent-polymer interactions that are therefore required to induce dissolution of these materials are provided by extremely protic solvents such as methane sulfonic acid and sulfuric acid. We believed that supercritical fluid based systems could be developed that would present similar solvation power without the negative aspects associated with strongly corrosive solvents.

A series of polymers were chosen containing many of the same strong interactions found in the above systems, but with reasonable solubilities in less difficult solvents such as m-cresol, formic acid, and N-methyl acetamide. The solvent system we have chosen is the lower organic alcohols, methanol and ethanol. This results from two factors. First, these solvents are polar and slightly protic and therefore might be able to provide some of the specific molecular interaction necessary to solvate highly polar and hydrogen bonded polymers. Second, each has an accessible supercritical temperature on the order of 240 °C. These temperatures are readily accessible under laboratory conditions. Polymers that we have found to be soluble in supercritical ethanol and methanol are poly( $\epsilon$ -caprolactam) (Nylon-6), poly(hexamethylene adipamide) (Nylon-66), poly(ethylene terephthalate) (PET), polycarbonate (PC), and poly(methyl methacrylate) (PMMA). Neither alcohol is a solvent for these polymers at room temperature in the absence of additional salts or acids. The nylons represent an especially attractive system for study since similar structure and crystallinity exist as for the aromatic polyamides.[4]

For the Nylon-66/methanol system a more extensive investigation performed to determine the solubilities as a function of temperature shows a great increase in the solubility as the critical temperature is reached. We believe that the same will be found for the other polymer systems. Rapid expansion of saturated Nylon/alcohol solutions from the high temperature/pressure conditions of a high pressure vessel results in the formation of high surface area, low density powders. Preliminary experiments indicate that rapid expansion of a solution containing two of the above polymers, such as Nylon-66 and polycarbonate, results in powders containing both polymer components as monitored by differential scanning calorimetry (DSC). The results were not conclusive and a molecularly blended system did not appear to be produced from the blending of a crystalline material with an amorphous polymer.



However, supercritical fluid produced powders of the neat or blended nylons could prove useful as starting materials in subsequent composite formation with heating cycles designed for selective annealing of the blend's components.

While these alcoholic solvent systems appear to possess great potential for processing of polymers requiring specific solvent-polymer interactions for dissolution, a previously unanticipated problem arises. At temperatures near the critical point the normally non-reactive alcohols become much more nucleophilic and initiate reactions with polymers containing ester or amide linkages. We believe that in addition to the dissolution of polymers such as nylon, PC, and PET, chain cleavage also occurs as evidenced by tacky or fluid product. The degree to which this occurs can readily be investigated using simple characterization techniques such as IR spectroscopy, viscosity, or light scattering on the resulting materials. In retrospect the solvent based reactions should have been predicted, given that the well known process for the production of poly(vinyl alcohol) is performed by the transesterification of poly(vinyl acetate) in hot methanol.[13] The enhanced reactivity of a supercritical solvent has also recently been effectively employed by a number of researchers who are utilizing the enhanced reactivity of supercritical water to perform oxidation reactions.[14]

Our original aim, the processing of normally difficult polymers, has been somewhat allusive however. While the dissolution of nylons and polyesters using alcohols is readily demonstrable we have as yet been unable to solubilize high performance polymers such as PPTA, PBI, PBO, Vectra polyaramides, or PPO. We believe that the degree to which specific interactions facilitate dissolution, such as protonation of PPTA in sulfuric acid producing a polyelectrolyte, cannot be duplicated in supercritical fluids. This is due to the inverse relationship between the protic nature of a solvent and its critical temperature. Solvents having low critical temperatures are non-polar, low molecular weight molecules, while more polar and protic solvents have extremely high critical temperatures, where solvent reactivity and difficulties associated with experimental apparatus arise. Therefore at pressures and temperatures where appreciable solubilities would be expected reaction as opposed to dissolution is the preferred pathway.

This is indeed the case when pushing a nucleophilic solvent such as methanol to high temperatures with even high performance polymers. For example, an initial report was given that a measurable degree of dissolution was

obtained for Vectra polyaramide. However the resulting material did not have the same good mechanical properties of the original material and therefore either represents a low molecular weight extraction product or a low molecular weight degradation product. Results on other high performance polymers indicate similar trends. Care should therefore be taken to ensure that extraction is not the only preferred mechanism at the conditions chosen.

Since the dissolution of high performance polymers does not appear to be amenable to processing using supercritical fluids as solvents, we have chosen to pursue a program of chemical modification of these polymers in order to enhance their solubilities. Following the method of Reynolds and coworkers, a series of modified PBIs have been prepared with chemically distinct side chains.[15] These side chains serve a twofold purpose. First, they should serve as chemical "handles" with which we can pull the polymers into solution provided that they have cohesive energy densities closely matched to that of the supercritical fluid. Second, they serve to disrupt the inherent crystallinity of the parent polymer there by making dissolution easier. We are currently screening such compounds in a series of different solvents. It must be noted however that these modifications will probably compromise some of the desired mechanical properties of the polymers.

In the context of polymer science supercritical fluids have perhaps their greatest utility in the processing of polymers not dominated by such strong cohesive interactions and whose cohesive energy density are matched to solvents whose critical pressures and temperatures are more readily accessible. For instance we have completed the preliminary stages of fiber production by rapid expansion of high/low density polyethylene (PE) and polypropylene (PP) from pentane at elevated temperatures and pressures through an appropriate nozzle. Fibers and ribbons of PE or PP in excess of several meters length have been produced. We have also been able to produce blended fibers of PE and PP. With proper nozzle design the fiber forming process could be better controlled to produce finer and more regular fibers.

We must note here that a qualitative difference has been observed in polyethylene fibers produced from sub critical and supercritical pentane. The fibers produced from expansion of a solution below the critical temperature are much more uneven and are more ribbon-like in appearance. Those produced above the critical point however are more regular. We believe that this difference results from the phase transition that occurs in the sub critical nozzle expansion

that does not occur in a supercritical solution. An expansion of a super heated liquid results in a liquid to gas transition that causes bubbling and fracture of the fiber. No such transition exists when employing a supercritical fluid.

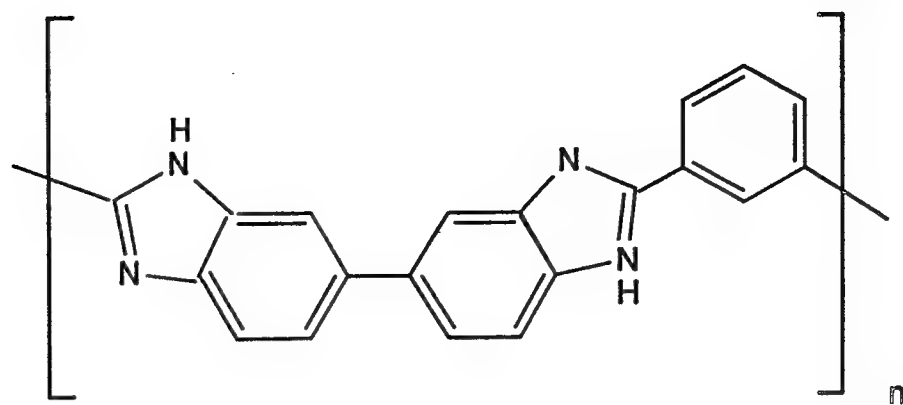
Construction of high pressure cells with windows appropriate for investigation of the phase behavior of the above systems has been completed. Phase diagrams for the above systems can be determined by observation of cloud points. The ability to perform dynamic light scattering and UV/Visible spectroscopy measurements has also been developed. With these techniques we will be better able to describe the behavior of the polymers under the supercritical conditions. Of particular interest is the investigation of the kinetics of the phase behavior during the initial pressure drop upon venting a solution to lower pressure through a nozzle. This initial phase transition may be the factor that controls the ultimate properties of materials produced. Preliminary measurements show that a clouding of a polyethylene/pentane solution occurs with only a very small pressure drop to a solution. The kinetics of this process may in fact determine the ultimate phase morphology of products produced in a supercritical fluid expansion.

We have also used these window cells to obtain information on the polymer dynamics in a supercritical fluid via dynamic light scattering. We therefore have an *in situ* means of monitoring molecular sizes, interactions, and perhaps distributions by examining diffusivity. This has been demonstrated in the pentane/low density polyethylene system over a range of temperatures and pressures. Careful control of temperature and pressure gradients is necessary however to extract meaningful results.

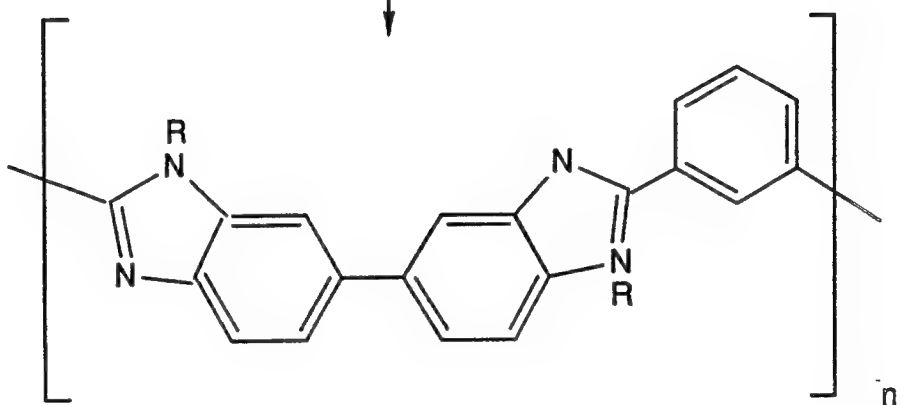
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4. "Engineering Plastics" in Encyclopedia of Polymer Science, Wiley Interscience, 6, 94 (1985)
5. "Aromatic Polyamides" in Encyclopedia of Polymer Science, Wiley Interscience, 11, 381 (1985).

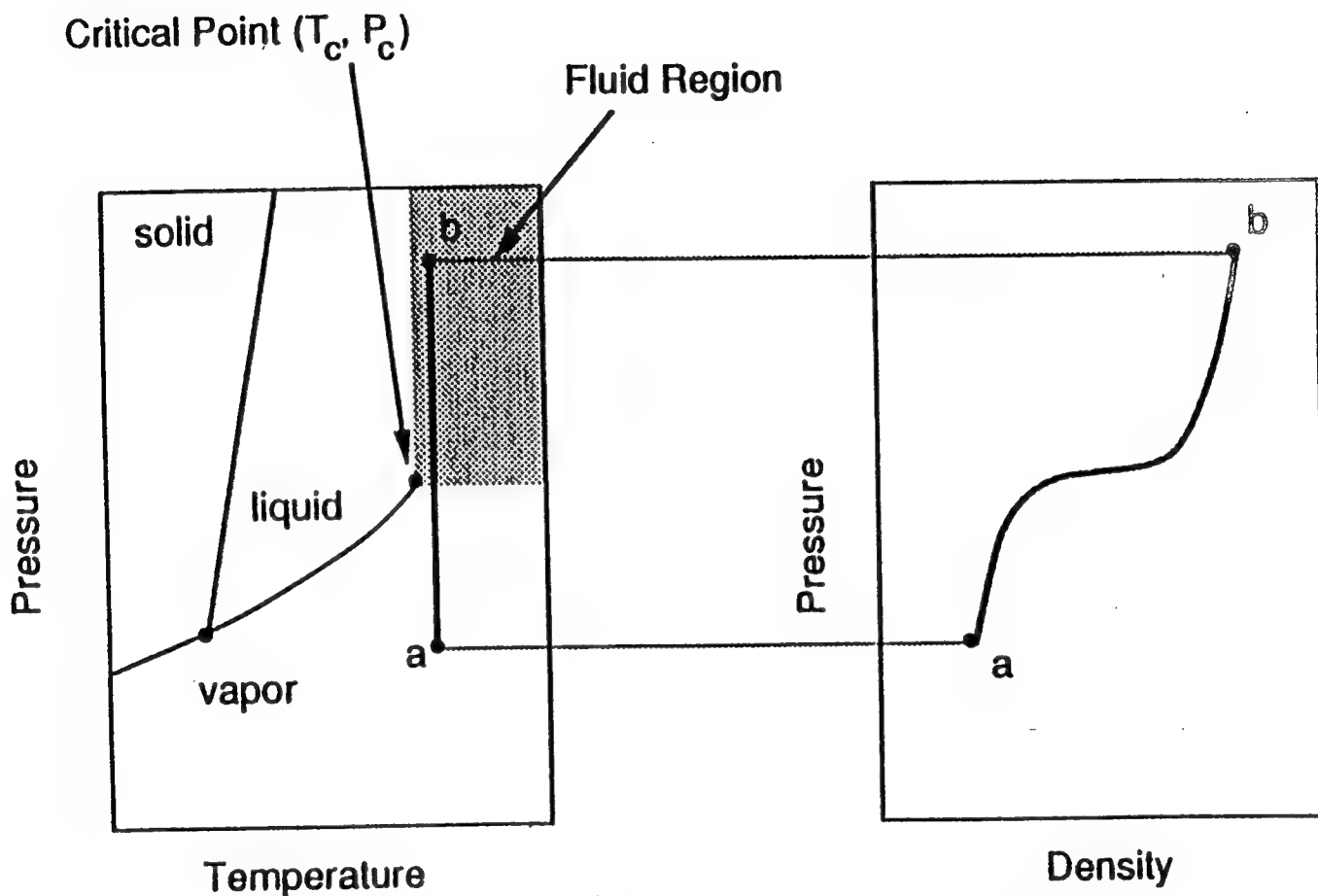
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15. Reynolds, personal communication.



$\text{RX (X=Cl, Br, I)}$   
 $\text{NaH, DMAc}$   
 $\text{reflux}$



## Solvent density in SCF region



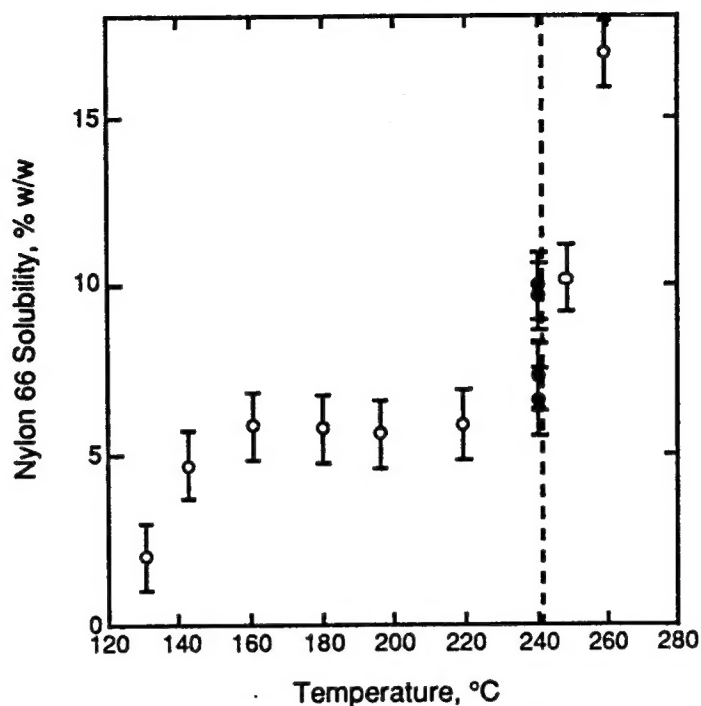
Pressure dependence on SCF density

Because solvating power of a fluid depends on its density, the solvating power of an SCF can be varied over a wide range by variations in pressure

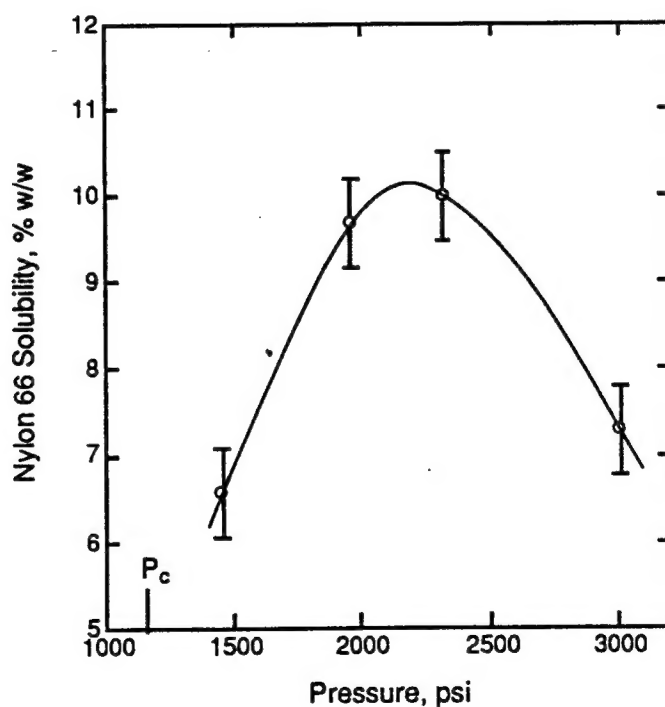
# "Primary" Pure Fluids

Fluid	Abbrev.	T/K	P/MPa	No. of mixtures
1. Helium 3	He <sub>3</sub>	3.311	0.115	1
2. Helium 4	He <sub>4</sub>	5.188	0.227	1
3. Hydrogen	H <sub>2</sub>	33.25	1.297	1
4. Neon*	Ne	44.40	2.654	1
5. Nitrogen*	N <sub>2</sub>	126.24	3.398	1
6. Carbon monoxide*	CO	132.85	3.494	1
7. Argon*	Ar	150.66	4.860	1
8. Oxygen*	O <sub>2</sub>	154.58	5.043	1
9. Methane*	CH <sub>4</sub>	190.55	4.595	11
10. Krypton	Kr	209.46	5.49	5
11. Carbon tetrafluoride	R14	227.6	3.74	1
12. Ethylene*	C <sub>2</sub> H <sub>4</sub>	282.35	5.040	10
13. Xenon	Xe	289.7	5.87	3
14. Chlorotrifluoromethane	R13	302.0	3.92	1
15. Carbon dioxide*	CO <sub>2</sub>	304.17	7.386	26
16. Ethane*	C <sub>2</sub> H <sub>6</sub>	305.34	4.871	17
17. Acetylene	C <sub>2</sub> H <sub>2</sub>	308.70	6.247	3
18. Nitrous oxide	N <sub>2</sub> O	309.15	7.285	3
19. Sulfur hexafluoride	SF <sub>6</sub>	318.82	3.765	1
20. Hydrogen chloride	HCl	324.55	8.263	3
21. Bromotrifluoromethane	R13B1	340.08	3.956	1
22. Propylene	C <sub>3</sub> H <sub>6</sub>	365.05	4.600	5
23. Chlorodifluoromethane	R22	369.27	4.967	4
24. Propane*	C <sub>3</sub> H <sub>8</sub>	369.85	4.247	21
25. Hydrogen sulfide	H <sub>2</sub> S	373.40	8.963	5
26. Trifluoropropylene	C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>	376.2	3.80	1
27. Dichlorodifluoromethane	R12	385.01	4.129	1
28. 1,1-Difluoroethane	R152a	386.44	4.520	1
29. Perfluorocyclobutane	c-C <sub>4</sub> F <sub>8</sub>	388.43	2.785	1
30. Dimethyl ether	Me <sub>2</sub> O	400.10	5.370	5
31. Ammonia	NH <sub>3</sub>	405.45	11.278	5
32. Isobutane*	i-C <sub>4</sub> H <sub>10</sub>	407.84	3.629	5
33. Dichlorotetrafluoroethane	R114	418.86	3.220	3
34. Perfluoro- <i>n</i> -pentane	n-C <sub>5</sub> F <sub>12</sub>	420.59	2.045	1
35. <i>n</i> -Butane*	n-C <sub>4</sub> H <sub>10</sub>	425.38	3.809	15
36. Sulfur dioxide	SO <sub>2</sub>	430.75	7.884	2
37. Vinyl chloride	C <sub>2</sub> H <sub>3</sub> Cl	432.00	5.670	1
38. Neopentane	neo-C <sub>5</sub> H <sub>12</sub>	433.75	3.196	2
39. Perfluorocyclohexane	c-C <sub>6</sub> F <sub>12</sub>	457.29	2.237	1
40. Isopentane*	i-C <sub>5</sub> H <sub>12</sub>	460.51	3.371	2
41. Diethyl ether	Et <sub>2</sub> O	466.56	3.651	1
42. <i>n</i> -Pentane*	n-C <sub>5</sub> H <sub>12</sub>	469.65	3.370	8
43. Perfluoro- <i>n</i> -heptane	n-C <sub>7</sub> F <sub>16</sub>	474.85	1.636	4
44. Epoxyp propane (propylene oxide)	—	482.25	4.924	1
45. Perfluoromethylcyclohexane	PFMCH	485.90	2.019	5
46. 2,2-Dimethyl butane	22DMB	489.25	3.102	2
47. 2-Methyl pentane*	2MP	498.05	3.035	2
48. 2,3-Dimethyl butane	23DMB	500.23	3.147	2
49. 3-Methyl pentane	3MP	504.62	3.128	2
50. <i>n</i> -Hexane*	n-C <sub>6</sub> H <sub>14</sub>	507.95	3.032	4
51. Acetone	Me <sub>2</sub> CO	508.15	4.758	2
52. Isopropanol	i-PrOH	508.31	4.764	1
53. Cyclopentane	c-C <sub>5</sub> H <sub>10</sub>	511.76	4.502	1
54. Methanol	MeOH	512.58	8.097	4
55. Ethanol	EtOH	516.25	6.384	2
56. Perfluorobenzene	C <sub>6</sub> F <sub>6</sub>	516.71	3.275	2
57. <i>n</i> -Propanol	n-PrOH	536.70	5.142	1
58. <i>n</i> -Heptane*	n-C <sub>7</sub> H <sub>16</sub>	540.00	2.736	6
59. Iso-octane (2,2,4-trimethylpentane)	i-C <sub>8</sub> H <sub>18</sub>	543.83	2.564	1
60. Acetonitrile	CH <sub>3</sub> CN	545.50	4.833	1
61. Cyclohexane	c-C <sub>6</sub> H <sub>12</sub>	553.54	4.075	2
62. Benzene	C <sub>6</sub> H <sub>6</sub>	562.24	4.888	9
63. <i>n</i> -Butanol	n-BuOH	562.89	4.416	3
64. <i>n</i> -Octane	n-C <sub>8</sub> H <sub>18</sub>	569.20	2.603	3
65. Methylcyclohexane	MCH	572.2	3.47	1
66. Toluene	—	591.79	4.109	2
67. Acetic acid	AcOH	592.71	5.786	1
68. <i>m</i> -Xylene	—	617.05	3.541	1
69. <i>n</i> -Decane	n-C <sub>10</sub> H <sub>22</sub>	619.3	2.096	4
70. Mesitylene	—	637.3	3.13	1
71. Water	H <sub>2</sub> O	647.29	22.09	3
72. <i>trans</i> -Decalin	—	687.1	2.615	1
73. Tetralin	—	719.2	3.515	1

# Nylon 6,6 in methanol

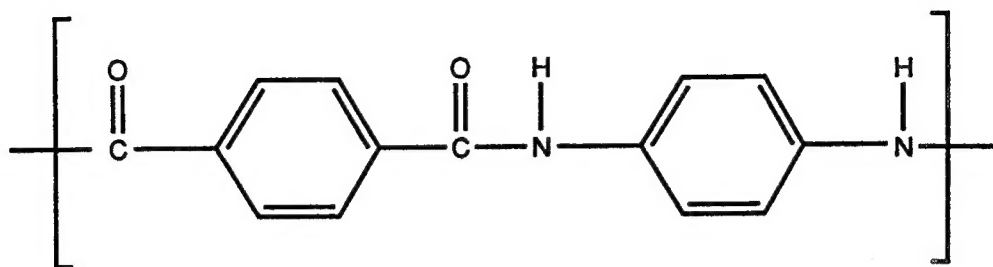


Solubility increases with temperature past the critical point

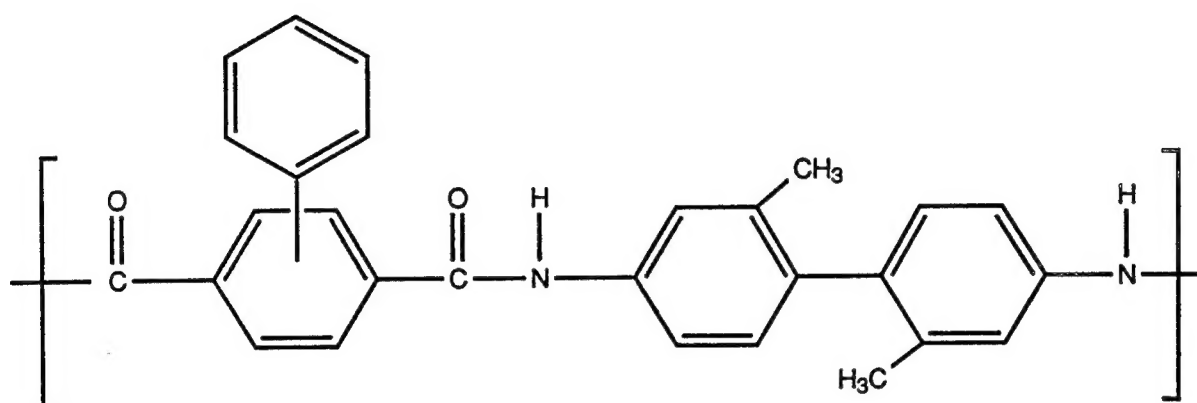


Maximum in solubility with pressure past the critical point



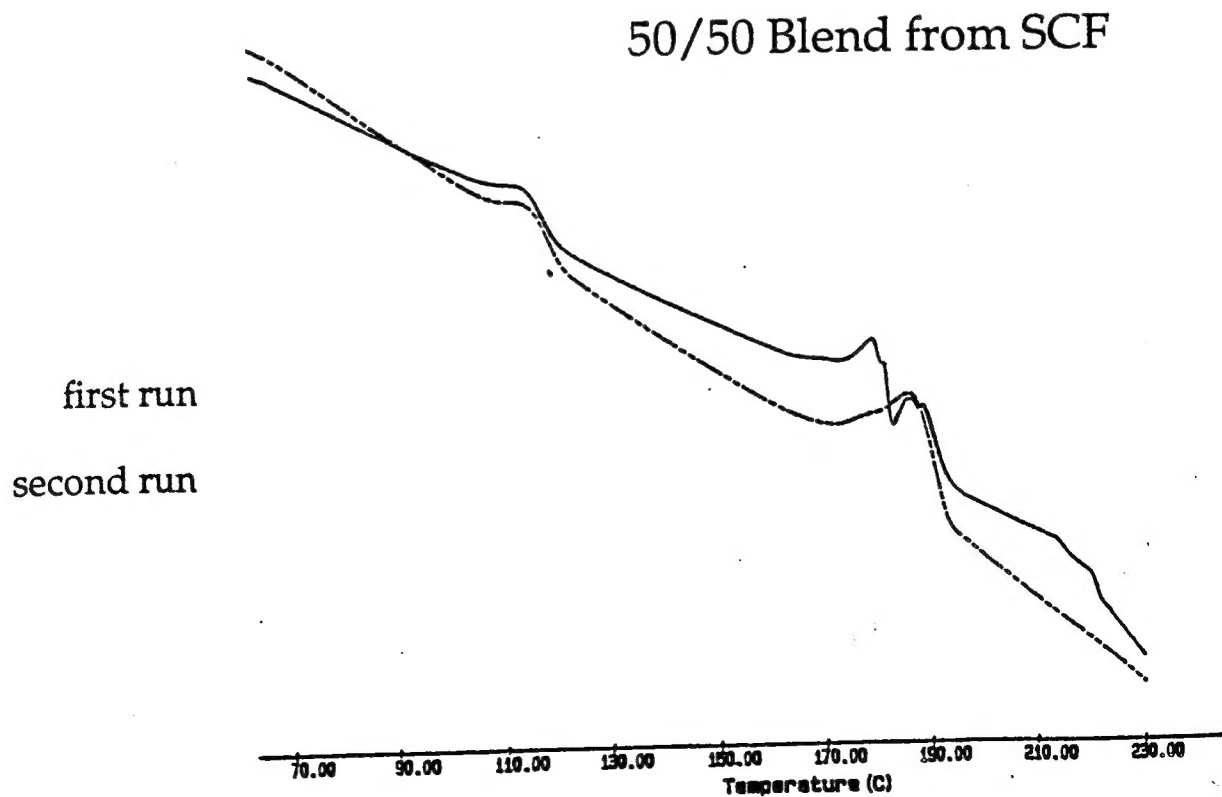
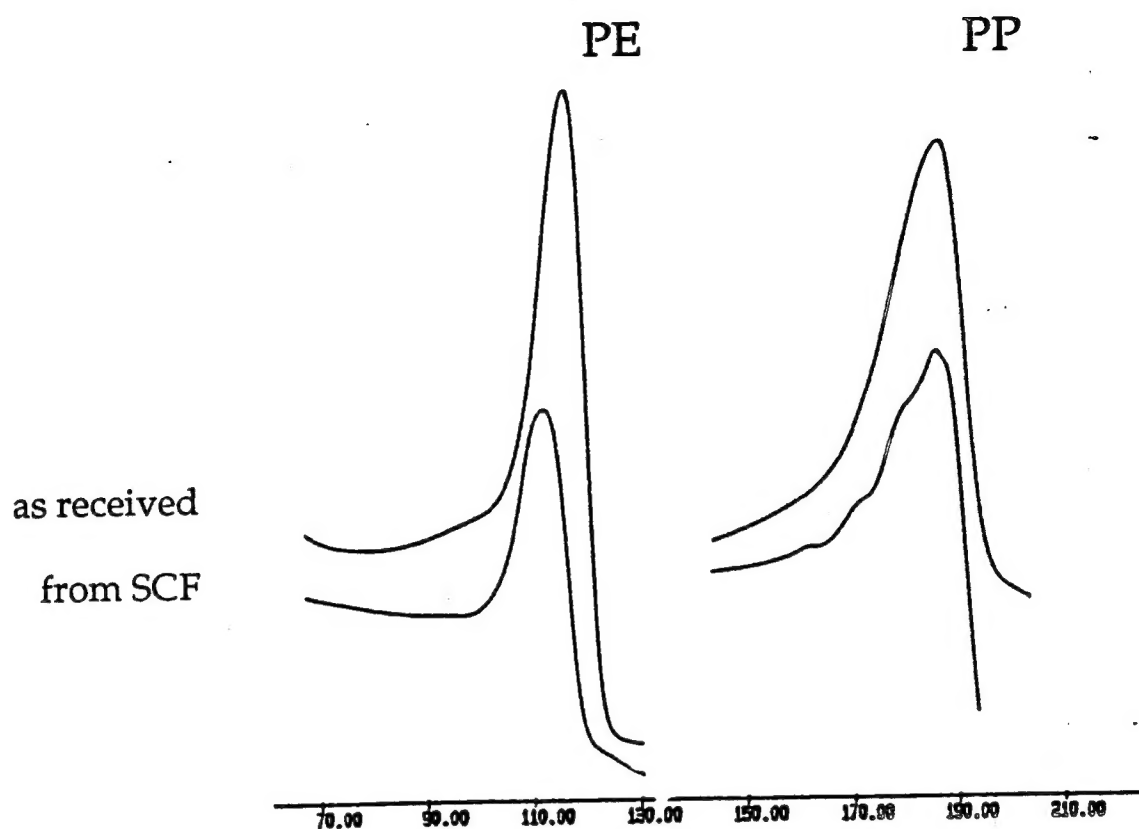


Kevlar

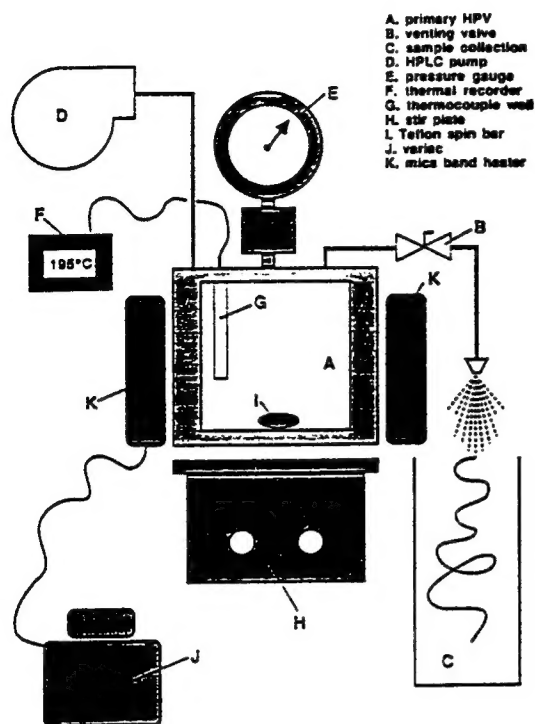


substituted polyaramides

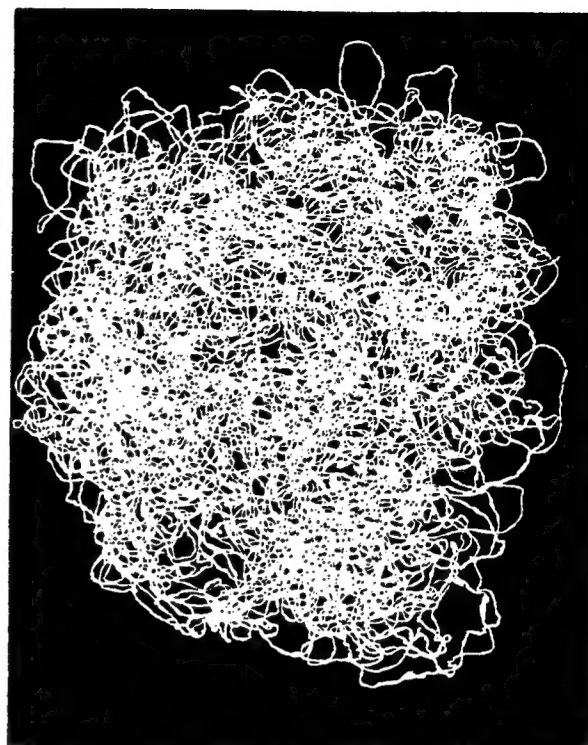
# DSC on PE, PP, and Blend



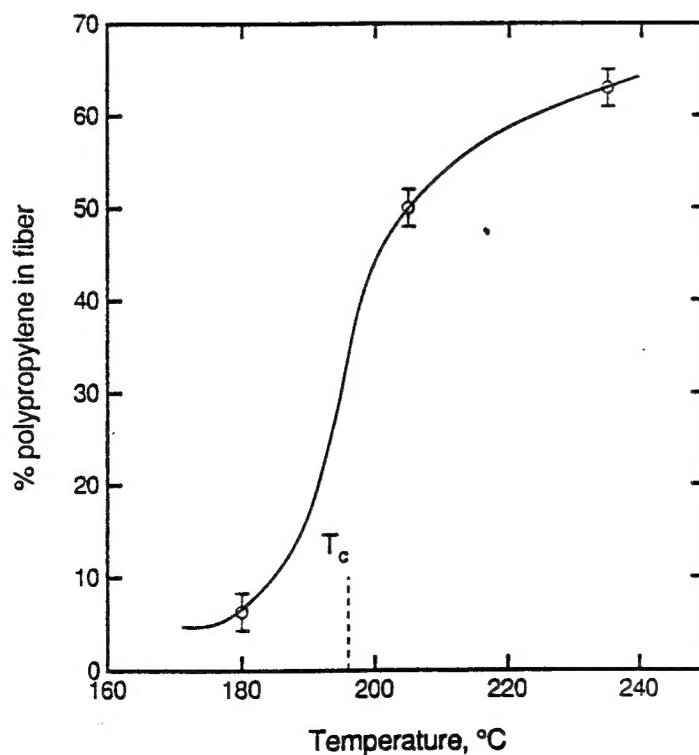
# Polymer Blending with Supercritical Fluids



SCF apparatus for  
fiber production



Polypropylene  
fiber mass



Composition of  
fiber spun from  
SCF blend of  
polypropylene  
and  
polyethylene